

## Thermodynamic Study of Binary Liquid Mixture of 1,2-dichlorobenzene in Tetrahydrofuran at T = 303.15 K

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### ABSTRACT

Thermodynamic parameters such as density ( $\rho$ ), ultrasonic speed ( $u$ ) and molar excess volume ( $V_m^E$ ) of binary mixture of 1,2-dichlorobenzene (DCB) in Tetrahydrofuran (THF) have been studied over the entire range of composition at 303.15 K. From these experimental results, parameters such as isentropic compressibility,  $K_s$ , interaction parameter,  $\chi_{12}$ , Flory parameters, coefficients,  $A_i$ , standard deviations,  $\sigma(Y^E)$ , and molar sound velocity,  $R_m$  have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic speeds have been analyzed in terms of Jacobson Free Length Theory (FLT), Schaaff's Collision Factor Theory (CFT), Nomoto's relation, and Van Dael's ideal mixture relation. Intermolecular Free Length,  $L_f$ , and available volume,  $V_a$ , have been calculated from FLT, CFT, and thermoacoustic approach for binary liquid system of 1,2-dichlorobenzene in THF at 303.15 K.

**Keywords:** Ultrasonic speed, excess molar volume, Schaaff's Collision Factor Theory, 1,2-dichlorobenzene, THF.

### INTRODUCTION

The measurement of thermodynamic and acoustic properties contributes to the understanding of the physicochemical

behavior of the binary and multi-component liquid mixtures. Excess properties of liquid systems, such as molar excess volume, are required for testing the theories of solutions, development of separation techniques and

equipment, and for other industrial applications. THF is the one of the most polar ethers with a wide liquid range, it is a useful solvent. Its main use, however, is as a precursor to polymers. The other main application of THF is as an industrial solvent for PVC and in varnishes. 1,2-dichlorobenzene is an organic solvent which finds use in number of industry. It is a versatile, high-boiling solvent. It is a preferred solvent for dissolving and working with fullerenes. Thus, a study of physical properties data on the binary mixture containing 1,2-dichlorobenzene and THF has attracted considerable interest in the literature<sup>1-3</sup>. Thus, 1,2-dichlorobenzene in THF mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover, literature survey indicates that no ultrasonic study on this binary system has been reported at 303.15 K. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary liquid mixture. Thus, a study of thermodynamic properties data on the binary mixture of 1,2-dichlorobenzene in THF has attracted considerable interest in our present study.

Research workers in the past have shown that NMR<sup>4, 5</sup>, IR<sup>6-7</sup> and Raman spectra<sup>8</sup>, have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves<sup>9-13</sup> and their absorption<sup>14, 15</sup> have already been found to be useful in the study of molecular interactions for inorganic, organic and organo-metallic binary systems. Likewise, researchers<sup>16-21</sup> have also employed

ultrasonic measurements to look into the important consequences of ion-solvent interactions for the structure of electrolytic solutions. References<sup>22, 23</sup> related to the field of medicine, whereas references<sup>24-27</sup> based on studies on emulsions/microemulsions, polymer surfactants interactions<sup>28</sup> and ultrasonic destruction of surfactants<sup>29</sup> are only a few cases to suggest versatility of the technique.

## EXPERIMENTAL

1,2- dichlorobenzene (CAS No. 95-50-1) was procured from Fischer Scientific Ltd. and are further purified by the methods given in Vogel text book of practical organic chemistry<sup>30</sup>. Prior to the experimental measurements, all the organic liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. The purities of all the samples determined by chromatographic analysis were better than 0.996 on a molar basis. Binary mixtures are prepared by mixing appropriate volumes of the liquid component in the specially designed glass bottles with air tight Teflon coated caps. The required properties are measured on the same day immediately after preparing each composition. The uncertainty in mole fraction is  $\pm 0.0001$ . A multi frequency digital micrometer reading ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) operating at 1, 2, 3 and 4 MHz was used to measure the ultrasonic velocity of the binary liquid mixtures (with an uncertainty of  $\pm 0.3$  %) at a constant temperature of 303.15 K by using a digital constant temperature water bath.

The temperature stability is maintained within  $\pm 0.001$  K by circulating thermostated water around the cell with a circulating pump connected to water bath. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (fifty) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance,  $d$  (cm) moved by the reflector is given by  $d = \frac{n\lambda}{2}$ ,

where  $\lambda$  is the wavelength.

The frequency  $\nu$ , of the crystal being accurately known (2.0 MHz), the speed of sound,  $u$  in  $\text{ms}^{-1}$  is calculated by using the relation  $u = \lambda\nu$ . Molar excess volume,  $V_m^E$  was calculated by specially designed double limbed glass dilatometer fitted with a microcapillary ( $\pm 0.01$  cm) in the centre. The density of solution was measured by a double arm pycnometer of bulb capacity 10 ml and a capillary of an internal diameter of about 1.0 mm. The mark of the stem was calibrated by double distilled water (conductivity less than  $1 \times 10^{-6}$   $\text{ohm}^{-1} \text{cm}^{-1}$ ) with 0.9970 and 0.9940  $\text{g cm}^{-3}$  as its density at 298.15 K and 303.15 K, respectively with buoyancy corrected. The accuracy of the density results was  $\pm 0.0001$  ( $\text{g cm}^{-3}$ ). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. The density and ultrasonic speed of binary mixtures were also measured by an Anton Paar Densitometer (DSA 5000). The accuracy of the density results was  $\pm 0.00001$  ( $\text{g/cm}^3$ ). Weight measurement were performed on a Mettler Toledo AB 135-S/FACT, single pan analytical balance, with

a precision of 0.01 mg. The densities, and ultrasonic speed,  $u$  of the pure liquids were in good agreement with the values found in the literature and are presented in Table 1.

## RESULTS

The molar excess volumes,  $V_m^E$ , of the solution were calculated from the densities of the pure liquids and their mixtures using the following equation [31]

$$V_m^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_{\text{mix}}} - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (1)$$

Where  $\rho_{\text{mix}}$  is the density of the mixture and  $x_1, M_1, \rho_1$  and  $x_2, M_2, \rho_2$  are the mole fraction, molar mass, and the density of pure component 1 and 2, respectively.

The following relations have been used to correlate the sound velocity,  $u$ , of the binary liquid mixtures:

Nomoto Relation<sup>32</sup>

$$u = \left( \frac{R_m}{V_{\text{mix}}} \right)^3 = \left( \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right)^3 \quad (2)$$

Where  $x_1, x_2, V_1, V_2$  and  $R_1, R_2$  are mole fractions, molar volumes, and molar sound velocity of first and second components, respectively.

Van Dael Relation<sup>33</sup>

$$\frac{1}{x_1 M_1 + x_2 M_2} \cdot \frac{1}{u_{\text{id.mix}}^2} = \frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \quad (3)$$

Where,  $M_1$ ,  $M_2$  and  $u_1$ ,  $u_2$  are the molar masses and sound velocities of first and second components, respectively, and  $u_{id.mix}$  is the ultrasonic velocity of the ideal mixture.

Jacobson's Free Length Theory (FLT)<sup>34</sup>

$$u_{mix} = \frac{K}{L_{f(mix.)} \rho_{mix}^{1/2}} \quad (4)$$

Where  $K$  is the Jacobson constant which is temperature dependent only and its value is 642.15 at 313.15 K. The  $L_{f(mix.)}$  is the intermolecular free length of the binary mixtures, which is given by  $L_f = \frac{2V_a}{Y}$ . Here

$V_a$  represents the available volume per mole and  $Y$  is the surface area per mole and these may be expressed as

$$V_a = (V_T - V_0) \quad (5)$$

$$Y = (36\pi N_A V_0^2)^{1/3} \quad (6)$$

Here  $N_A$  is the Avogadro's number and  $V_0$  and  $V_T$  are the molar volumes at zero Kelvin and at temperature  $T$ , respectively. The  $V_0$  can be obtained from the following relation using critical temperature  $T_c$ :

$$V_0 = V_T \left( 1 - \frac{T}{T_c} \right)^{0.3} \quad (7)$$

The critical temperature,  $T_c$  is the mole fraction additive of the values of its pure components and is given by the relation:

$$T_c = x_1 T_{c(1)} + x_2 T_{c(2)} \quad (8)$$

The thermodynamic intermolecular free lengths,  $L_f$ , in the binary liquid mixtures have been calculated using the relation:

$$L_f = 2 \frac{[V_T - \{x_1 V_{0(1)} + x_2 V_{0(2)}\}]}{(x_1 V_1 + x_2 V_2)} \quad (9)$$

The ultrasonic intermolecular free lengths  $L_f$ , have also been computed using the Schaaff's relation for available volume ( $V_a$ ):

$$V_a = V_T \left[ 1 - \frac{u}{u_\infty} \right] \quad (10)$$

Where,  $u$  is the ultrasonic velocity at temperature  $T$  and  $u_\infty$  is 1600 m.s<sup>-1</sup>.

Schaaff's Collision Factor Theory (CFT)<sup>35-36</sup>

$$u_{mix} = u_\infty (x_1 s_1 + x_2 s_2) \frac{[x_1 b_1 + x_2 b_2]}{V_{mix}} \quad (11)$$

Where,  $b$  and  $s$  are the geometric volume and collision factor, respectively. The actual volume of the molecule per mole of the liquid has been computed using the relations

$$b = \frac{4}{3} \pi r^3 N \quad (12)$$

Where,  $r$  is the molecular radius which has been computed using the Schaaff's relation<sup>36</sup>

$$r = \left( \frac{M}{\rho N} \right)^{1/3} \left[ \frac{3}{16\pi} \left[ 1 - \frac{\gamma RT}{Mu^2} \left( \sqrt{1 + \frac{Mu^2}{3\gamma RT}} - 1 \right) \right] \right]^{1/3} \quad (13)$$

$$b' = \left[ \frac{M}{\rho} - \frac{\gamma RT}{\rho u^2} \left( \left( 1 + \frac{Mu^2}{3\gamma RT} \right)^{\frac{1}{2}} - 1 \right) \right] \quad (14)$$

$$r = \left( \frac{3b'}{16\pi N} \right)^{\frac{1}{3}} \quad (15)$$

Where,  $b'$  is the van der Waal's constant and is equal to four times the actual volume of the molecules per mole of the liquid, i.e.  $b' = 4b$ .

The thermoacoustical method<sup>37-39</sup> has also been employed to obtain the available volume,  $V_a$  using the relation

$$V_a = V_T \left( \frac{1}{K' + 1} \right) = V_T \left( \frac{1}{K'' + K' + 1} \right) \quad (16)$$

The  $K'$ ,  $K$ , and  $K''$  are known as isothermal, isobaric and isochoric acoustical parameters, respectively, and can be expressed by the relation

$$K' = K + K'' = \frac{1}{2} \left[ 3 + \frac{S^* (1 + \alpha T) + X}{\alpha T} \right] \quad (17)$$

$$K'' = 1 + \frac{X}{2\alpha T} \quad (18)$$

$$K = \frac{1}{2} \left[ 1 + \frac{S^* (1 + \alpha T)}{\alpha T} \right] \quad (19)$$

$$S^* = 1 + \frac{4\alpha T}{3} \quad (20)$$

The  $X$  is known as the isobaric temperature coefficient of internal pressure and can be expressed as

$$X = 2 \frac{(1 + 2\alpha T)}{\tilde{V}^{C_1}} \quad (21)$$

Where  $\tilde{V}$  represents the reduced molar volume and  $C_1$  is the Moelwyn-Hughes parameter and can be expressed as

$$\tilde{V} = \left[ \frac{\alpha T / 3}{1 + \alpha T} + 1 \right]^3 \quad (22)$$

$$C_1 = \frac{13}{3} + \frac{1}{\alpha T} \frac{4\alpha T}{3} \quad (23)$$

The thermal expansion coefficient,  $\alpha$ , has been calculated using the equation:

$$\alpha = \left( \frac{1}{\rho} \right) \left( \frac{\partial \rho}{\partial T} \right)_p \quad (24)$$

The isentropic compressibility has been calculated from Newton-Laplace's equation

$$k_s = \frac{1}{\rho u^2} \quad (25)$$

The excess isentropic compressibility was found out by using the relation,

$$k_s^E = k_s - k_s^{id} \quad (26)$$

Where,  $k_s^{id}$  the isentropic compressibility for the ideal mixture, was obtained according to Benson and Kiyohara<sup>40</sup> and Acree<sup>41</sup>:

$$k_s^{id} = \sum_i \phi_i \left[ k_{s,i} + \frac{TV_i \alpha_i^2}{C_{p,i}} \right] - T \left( \sum_i x_i V_i \right) \frac{\left( \sum_i \phi_i \alpha_i \right)^2}{\left( \sum_i x_i C_{p,i} \right)} \quad (27)$$

Where,  $\phi_i$  is the volume fraction of component  $i$  in the mixture,  $x_i$  is the corresponding mole fraction,  $T$  is the absolute temperature, and  $k_{s,i}$ ,  $V_i$ ,  $\alpha_i$  and  $C_{p,i}$  are the isentropic compressibility, the molar volume, the cubic expansion coefficient, and the molar heat capacity of pure components respectively. The cubic expansion coefficients were obtained from experimental density measurements performed in our laboratory at different temperatures.

The excess isentropic compressibility of the binary mixture were fitted with a Redlich-Kister polynomial equation<sup>42</sup>

$$k_s^E = x_1 x_2 \sum_{j=0}^n A_j (x_1 - x_2)^j \quad (28)$$

Where,  $A_j$  are the adjustable parameters.

Oswal<sup>43</sup> extended the Prigogine-Flory-Patterson (PFP) theory to estimate the isentropic compressibility's and speeds of sound of liquid mixtures. At a given temperature,  $T$ , the PFP theory can be used to calculate the molar volumes,  $V$  and the molar heat capacities,  $C_p$ , of a liquid mixture if the interaction parameter,  $\chi_{12}$ , is known.

Inter molecular free length and relative association has been calculated by the following formula:

$$L_f = K (K_s)^{1/2} \quad (29)$$

$$R_A = \frac{\rho}{\rho_0} \left( \frac{u_0}{u} \right)^{1/3} \quad (30)$$

Where  $\rho_0$  and  $u_0$  are the densities and ultrasonic speed of pure solvent,  $\rho$  and  $u$  are the density and ultrasonic speed of mixture respectively and  $K$  is the temperature dependent Jacobson constant ( $6.0816 \times 10^4$  at  $35^\circ \text{C}$ ).

The deviation parameters of binary liquid mixtures have been evaluated using the general equation:

$$\Delta Y = Y_{\max} - (X_1 Y_1 + X_2 Y_2) \quad (31)$$

Where,  $Y$  indicates the parameter such as isentropic compressibility, inter molecular free length and ultra sonic speed.  $X_1$  and  $X_2$  are the mole fraction of component 1 and 2 respectively.  $\Delta Y$ ,  $Y_1$ ,  $Y_2$ , and  $Y_{\max}$  are the deviation parameter, parameters of the component 1 and 2 and observed parameters, respectively.

The number of contact sites per segment of a molecule, has been estimated using Bondi's method<sup>44</sup>. Molecular interaction parameter for each binary mixture was obtained by fitting the PFP theory to the corresponding experimental equimolar  $H^E$  values<sup>45-46</sup>. Once the

interaction parameter is obtained, the isentropic compressibility and the speed of sound can be estimated.

Physical properties of pure substance like density, ultrasonic speed at 303.15 K are shown in Table 1. Speeds of sound,  $u$ , density, isentropic compressibility,  $k_s$ , and deviation in speed of sound of binary liquid mixture of 1,2-dichlorobenzene in THF over the different composition range at a temperature of 303.15 K are reported in Table 2. Values of deviation in isentropic compressibility's,  $\Delta K_s$ , intermolecular free length,  $L_f$ , and relative association,  $R_a$ , of the binary liquid mixture is shown in Table 3. Table 4 shows molar excess volume of the binary liquid mixture of 1,2- dichlorobenzene in THF at 303.15 K. Table 5 shows Intermolecular Free Length,  $L_f$ , calculated from free length theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP) for 1,2-dichlorobenzene in THF. Table 6 shows available volume,  $V_a$ , calculated from FLT, CFT, and TAP for 1,2-dichlorobenzene in THF at 303.15 K.

The values of the coefficients of Redlich-Kister polynomial equation for all the binary mixtures along with values of the standard deviation are represented in Table 7 for 1,2-dichlorobenzene in THF binary liquid mixture at 303.15 K. Flory parameters<sup>47, 48</sup> of the pure compounds along with their physical properties are given in Table 8 for 1,2-dichlorobenzene in THF binary liquid mixture at 303.15 K. Table 9 gives the estimated and experimental

equimolar,  $u$  and  $k_s$ , values along with the interaction parameter,  $\chi_{12}$ , for 1,2-dichlorobenzene in THF binary liquid mixtures at 303.15 K. Table 10 gives theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's and Van Dael and Vangeel's ideal mixing relation and percentage error in calculated values for 1,2-dichlorobenzene in THF at 303.15 K.

## DISCUSSION

Binary systems of 1,2-dichlorobenzene in THF shows negative deviation through  $\Delta K_s$  isotherms over entire range of mole fraction. A clear minima at the mole fraction around  $x_1 = 0.4$ , indicates that the maximum interactions are at that this mole fraction range. From Table 2 & 3, it is observed that  $\Delta u$  values are positive while,  $\Delta K_s$  values are negative, such trends of positive deviation in a speed of sound and negative deviation in isentropic compressibility is quite common<sup>49-52</sup>.

In pure 1,2-dichlorobenzene, there is dipole-dipole as well as the usual dispersive interaction. The effect of adding a polar second component is primarily to disrupt the dipolar interaction of the first component, but when the second component is also polar, the dipole-dipole interaction between unlike molecule is most likely which result in contraction of volume and the mixture becomes the less compressible<sup>53-54</sup>.

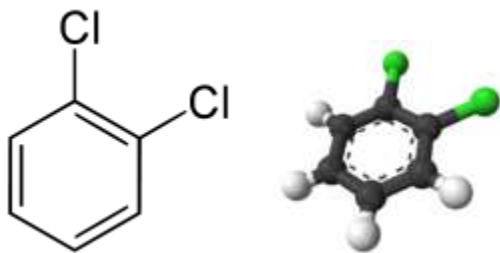


Figure 1 Structure of 1,2-dichlorobenzene.

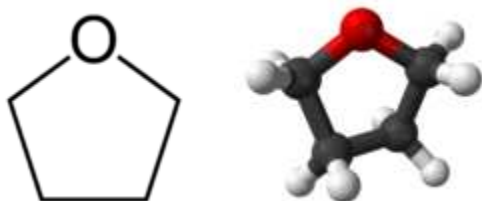


Figure 2 Structure of Tetrahydrofuran.

The behavior of binary liquid mixture can be explained in term of 1) physical forces -dispersion 2) chemical forces – dipole-dipole interaction. The former factor increases the intermolecular free length as described by Jacobson<sup>54</sup>. This in turn, causes negative deviation in sound speed and positive deviation in compressibility. On the other hand, the latter factor decreases the intermolecular path lengths leading to a positive deviation in sound speed and negative deviation in compressibility and excess molar volume,  $V_m^E$ . The actual values depend upon the relative strength of two opposing effects. The observed negative values of  $\Delta K_s$  and excess molar volume (Table 4) and positive values of  $\Delta u$  for these mixtures imply that the specific interaction dominates over the dispersive interaction between unlike molecules. From Table 5, the negative value

of deviation in the molecular free length parameter substantiates the above argument undoubtedly and undeniably unveils the fact that the specific interaction is being operative between the molecules of solvent and co-solvents in the mixture.

Since,  $V_m^E$  is a packing effect and  $H_m^E$  is an interactional effect between the A and B constituents of an (A+B) mixture and as  $V_m^E$  data of the 1,2- dichlorobenzene in THF binary mixtures are negative throughout the composition range of THF, this suggests that as compared to the dispersion forces, negative value of  $V_m^E$  in general, always cause more compact packing of the molecules due to stronger dipole-dipole chemical interaction between the two unlike organic solvents. Their respective contribution to the measured data is a function of the mole fraction of THF.

The conclusion is further fortified by the increasing value of relative association,  $R_A$  included in Table 3. All the trends of the above parameters indicate that the mixtures are less compressible than their corresponding ideal mixtures. Generally, the deviation parameter is considered to be the reflecting agents of the magnitude of polarity at the site of interaction in the molecules<sup>55</sup>.

The intermolecular free length,  $L_f$ , can be related to the space filling ability assuming that the molecules are incompressible hard spheres having uniform radius. The intermolecular free length,  $L_f$ , obtained using free length theory (FLT) for the (1,2- dichlorobenzene + THF) decreases with the increase in mole fraction of THF



(Table 5). However, the  $L_f$  value obtained from Schaaf's collision factor theory (CFT) increases with the increase in the mole fraction of THF. The change in the slope of the isotherms of  $L_f$  as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to disruption of dipole-dipole interactions between like polar molecules. However, the thermoacoustic approach (TAP) predicts that the  $L_f$  values in these binary mixtures decrease with increase in the mole fraction of THF. The  $L_f$  values for these binary mixtures obtained from the ultrasonic methods are higher than those obtained from the free length theory and the thermoacoustical approach.

The available volume,  $V_a$ , obtained using Free Length Theory (FLT) for the (1,2- dichlorobenzene + THF) decreases with the increase in mole fraction of 1,2-dichlorobenzene (Table 6). However, the  $V_a$  value obtained from Schaaf's Collision

Factor Theory (CFT) increases with the increase in the mole fraction of THF. The change in the slope of the isotherms of available volume as a function of mole fraction in the higher mole fraction region predicted by FLT and CFT shows that the entropy effect related to the structural rearrangement of solvent molecules due to stronger dipole-dipole interactions between unlike molecules of 1,2- dichlorobenzene in THF. However, the thermoacoustic approach (TAP) predicts that the  $V_a$  values in these binary mixtures decrease with increase in the mole fraction of THF.

The study of standard deviations,  $\sigma(k_s^E)$ , presented in Table 7, reveals that the results of ultrasonic velocity for 1,2-dichlorobenzene with THF systems can be satisfactorily explained by Van Deal Ideal Mixture relation (minimum  $< 0.1$ ). Stronger dipolar interaction between unlike polar organic solvents is also justified by the values of interaction parameters (Table 9). Values of interaction parameters are low for 1,2- dichlorobenzene in THF which suggest dipole-dipole interaction between the unlike polar organic solvents.

**Table 1. Comparison of experimental densities,  $\rho$  of pure liquids with literature values at 298.15 K, ultrasonic speed,  $u$  and molar volume,  $V^0$  at 303.15 K.**

Components	$\rho$ (g cm <sup>-3</sup> )		$u$ (m s <sup>-1</sup> )		$V^0$ (cm <sup>3</sup> mol <sup>-1</sup> ) at 303.15K [58]
	Expt.	Lit.	Expt.	Lit.	
THF	0.8896	0.8882[56]	1258	1254	114.3
1,2- dichlorobenzene	1.3012	1.3022 [57]	1145#	1137# [57]	58.2

# value at 298.15K

Theoretical values of ultrasonic speed calculated from FLT theory shows large percentage error in 1,2-dichlorobenzene with THF binary liquid mixtures at 303.15 K (Table 10). Theoretical

values of ultrasonic speed calculated from Nomoto's and Van Dael and Vangeel's ideal mixing relations are almost identical. These relations show minimum percentage error in theoretical ultrasonic speed.

**Table 2. Values of density,  $\rho$  speed of sound and deviation in speed of sound,  $\Delta u$  of binary liquid mixture at 303.15 K.**

Mole Fraction ( $x_1$ )	$\rho$ (g cm <sup>-3</sup> )	$u$ (m s <sup>-1</sup> )	$\Delta u$ (m s <sup>-1</sup> )
<b>THF (1) + 1,2- dichlorobenzene (2)</b>			
0.0000	0.8896	1258.00	0.000
0.0692	0.9321	1230.00	17.23
0.1492	0.9965	1220.00	24.43
0.1999	1.0834	1211.00	25.81
0.2963	1.1476	1203.00	27.22
0.3774	1.1781	1185.00	29.23
0.4257	1.1938	1170.00	31.65
0.5985	1.2359	1162.00	27.35
0.6991	1.2668	1155.00	22.23
0.8895	1.2848	1150.00	14.12
1.0000	1.3012	1145.00	0.000

**Table 3. Values of deviation in isentropic compressibility  $\Delta K_s$ , intermolecular free length,  $\Delta L_f$  and relative association ( $R_A$ ) of sound of binary liquid mixture at 303.15 K.**

Mole Fraction ( $x_1$ )	$-\Delta K_s$ (10 <sup>-11</sup> Pa <sup>-1</sup> )	$-\Delta L_f$ (10 <sup>-11</sup> m)	( $R_A$ )
<b>THF (1) + 1,2- dichlorobenzene (2)</b>			
0.0000	00.00	0.0000	-
0.0862	08.16	2.2341	1.0047
0.1335	09.31	2.8879	1.0123
0.1867	11.43	3.2534	1.0245
0.2766	14.93	3.8180	1.0364
0.3499	16.14	4.2645	1.0408
0.4889	14.04	3.7785	1.0538
0.5654	11.29	3.4212	1.0634
0.6985	09.41	2.3405	1.0713
0.8854	06.69	1.6350	1.0837
1.0000	00.00	0.0000	-

**Table 4. Molar excess volumes,  $V_m^E$  (cm<sup>3</sup> mol<sup>-1</sup>) of the binary liquid mixtures at 303.15 K.**

$x_1$	$-V_m^E$ (Theoretical)	$-V_m^E$ (Experimental)
<b>1,2- dichlorobenzene (2) + THF (1)</b>		
0.0851	0.0546	0.051
0.2567	0.1473	0.149
0.2869	0.1582	0.156
0.3265	0.1765	0.174
0.3758	0.1938	0.192
0.4625	0.2406	0.243
0.5687	0.2587	0.256
0.6578	0.1705	0.173
0.6874	0.1053	0.103
0.7348	0.0827	0.084
0.8224	0.0559	0.057
0.8847	0.0414	0.042
0.9367	0.0286	0.027

**Table 5. Intermolecular Free Length ( $-L_f$ ), calculated from Free Length Theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP) for binary mixtures at 303.15 K.**

$x_1$	$-L_f(FLT)/nm$	$-L_f(CFT)/nm$	$-L_f(TAP)$
<b>1,2- dichlorobenzene (2) + THF (1)</b>			
0.0756	0.0732	0.0725	0.0665
0.1137	0.0756	0.0751	0.0644
0.1865	0.0678	0.0680	0.0654
0.2759	0.0610	0.0631	0.0678
0.3857	0.0574	0.0541	0.0682
0.5215	0.0560	0.0553	0.0636
0.6057	0.0554	0.0603	0.0567
0.6879	0.0541	0.0632	0.0548
0.7869	0.0536	0.0601	0.0578
0.8875	0.0528	0.0721	0.0546
0.9567	0.0522	0.0735	0.0532

**Table 6. Available Volume,  $V_a$ , calculated from Free Length Theory (FLT), Collision Factor Theory (CFT), and Thermoacoustic Approach (TAP) for binary mixtures at 303.15 K.**

$x_1$	$V_a \cdot 10^6 (FLT) / (m^3 \cdot mol^{-1})$	$V_a \cdot 10^6 (CFT) / (m^3 \cdot mol^{-1})$	$V_a \cdot 10^6 (TAP) / (m^3 \cdot mol^{-1})$
<b>1,2- dichlorobenzene (2) + THF (1)</b>			
0.0735	22.2587	19.5476	23.2431
0.1356	21.5687	19.8416	23.1327
0.2248	21.1453	19.5462	22.7814
0.2724	21.0568	20.1257	22.2754
0.3685	20.8940	20.5487	22.0204
0.4356	20.7524	21.2587	21.8796
0.5678	20.6671	21.5632	21.3980
0.6587	20.5574	22.2440	21.0370
0.7469	20.4157	22.4613	20.7506
0.8624	20.2756	22.5721	20.3434
0.9341	19.8438	22.8609	20.3014

**Table 7. Values of parameters  $A_j$  of the Redlich-Kister equation and corresponding standard deviations,  $\sigma(k_s^E)$  for the binary systems at 303.15 K.**

$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(k_s^E) (T Pa^{-1})$
<b>1,2- dichlorobenzene (2) + THF (1)</b>				
63.2	-29.10	7.30	-11.40	0.11

**Table 8. Physical properties reduced molar volume  $\tilde{V}$ , critical pressure  $P^*$  and Flory parameters isothermal compressibility,  $k_T$  collision factor,  $s$  of the pure compounds at 303.15K.**

Compound	$k_T (T Pa^{-1})$	$\tilde{V}$	$P^* (J cm^{-3})$	$s (A^{\circ-1})$
<b>1,2- dichlorobenzene</b>	654.7	1.57	568.6	1.11
<b>THF</b>	987.4	1.13	425.3	1.01

**Table 9. Interaction Parameters,  $\chi_{12}$ , calculated and experimental equimolar speed of sound, and isentropic compressibilities,  $k_s$ , of the binary systems at 303.15 K.**

$\chi_{12}$ ( $J\ cm^{-3}$ )	$u_{cal}$ ( $m\ s^{-1}$ )	$u_{exp}$ ( $m\ s^{-1}$ )	$k_s$ ( $T\ Pa^{-1}$ )	$k_{s,exp}$ ( $T\ Pa^{-1}$ )
<b>1,2- dichlorobenzene + THF</b>				
93.7	1166.26	1161.27	11.25	11.17

**Table 10. Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's (NOM) and Van Dael and Vangeel's ideal mixing relation (VD) and percentage error in calculated values for 1,2- dichlorobenzene (2) + THF (1) at 303.15 K.**

$x_1$	$u$ ( $m\ s^{-1}$ )				% error			
	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
0.0000	1145.0	1145.0	1145.0	1145.0	0.00	0.00	0.00	0.00
0.0864	1152.6	1150.7	1149.6	1151.2	1.87	1.08	1.02	1.09
0.1624	1171.3	1162.3	1154.3	1157.7	2.18	0.62	0.17	0.05
0.3452	1191.2	1171.4	1162.1	1165.4	3.30	0.93	0.11	0.00
0.4526	1198.6	1178.6	1172.8	1174.3	4.76	0.96	0.00	0.08
0.5567	1205.7	1185.7	1180.2	1180.8	5.04	0.84	0.10	0.18
0.6587	1215.4	1191.3	1187.5	1191.6	4.91	0.75	0.15	0.22
0.7563	1222.6	1197.7	1196.4	1198.5	4.86	0.62	0.19	0.25
0.8452	1237.1	1215.8	1206.4	1210.6	3.41	0.38	0.18	0.23
0.9368	1240.3	1234.4	1228.9	1234.4	2.07	0.29	0.17	0.19
1.0000	1256.0	1256.0	1256.0	1256.0	0.00	0.00	0.00	0.00

## CONCLUSION

Density ( $\rho$ ), ultrasonic velocity ( $u$ ) and excess molar volume ( $V_m^E$ ) of binary mixtures of 1,2-dichlorobenzene in THF have been measured over the entire range of composition and at 303.15 K. From these experimental results, parameters such as deviation in isentropic compressibility,  $\Delta K_s$ , interaction parameter,  $\chi_{12}$ , Flory parameters, Coefficients  $A_i$ , standard deviations,  $\sigma(Y^E)$  and molar sound speed,  $R_m$  have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equations. The experimental ultrasonic velocities have been analyzed in terms of Nomoto's relation, Van Dael's ideal mixture relation, Jacobson free length theory and Schaaff's collision factor theory. Intermolecular free length,  $L_f$ , and available volume,  $V_a$ , have been calculated from Jacobson free length theory, Schaaff's collision factor theory, and thermoacoustic approach for binary systems of 1,2-dichlorobenzene in THF at 303.15 K. The observed negative values of  $\Delta K_s$  and excess molar volume  $V_m^E$  and positive values of  $\Delta u$  for these mixtures imply that the specific chemical dipole-dipole interactions dominate over the physical dispersive interaction between unlike organic polar solvents.

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